VOLTAMMETRY in 21st Century- Theory, Experiments and Future Perspectives

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VOLT-AM-METRY: is an electrochemical technique where information about an analyte is obtained by measuring current (I) as a function of *applied* potential (E)

in these techniques only a micro molar or smaller amount of sample (analyte) is used

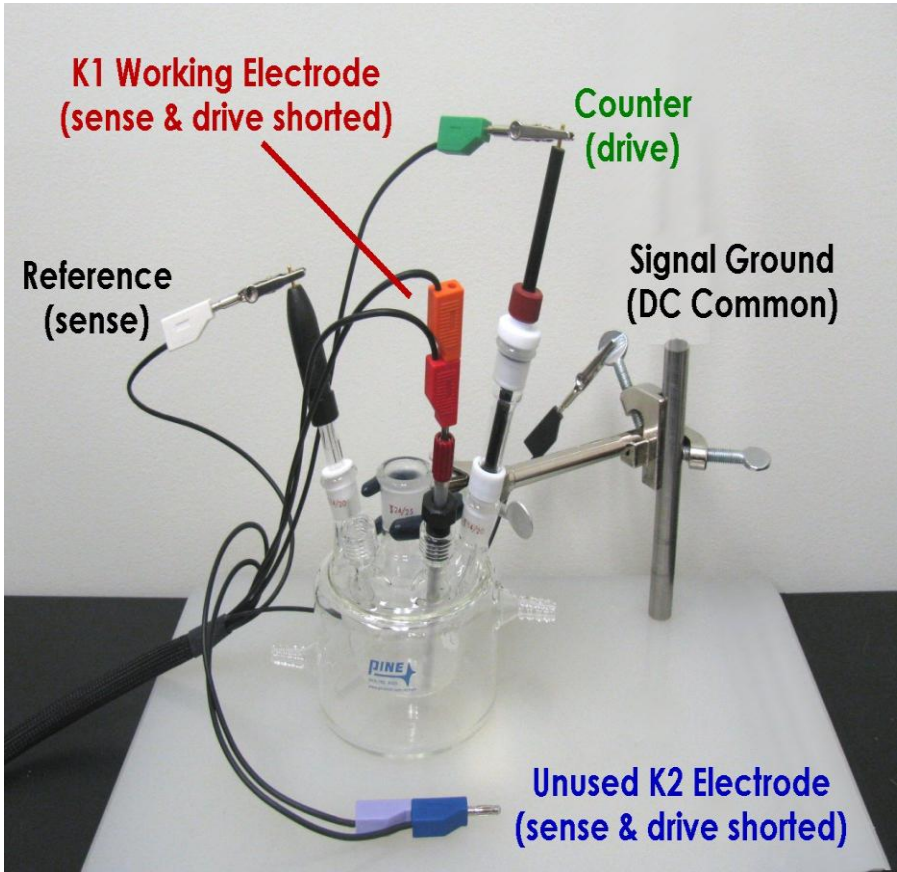
Instrumentation – Three electrodes are submerged in electrolyte solution containing a given analyte

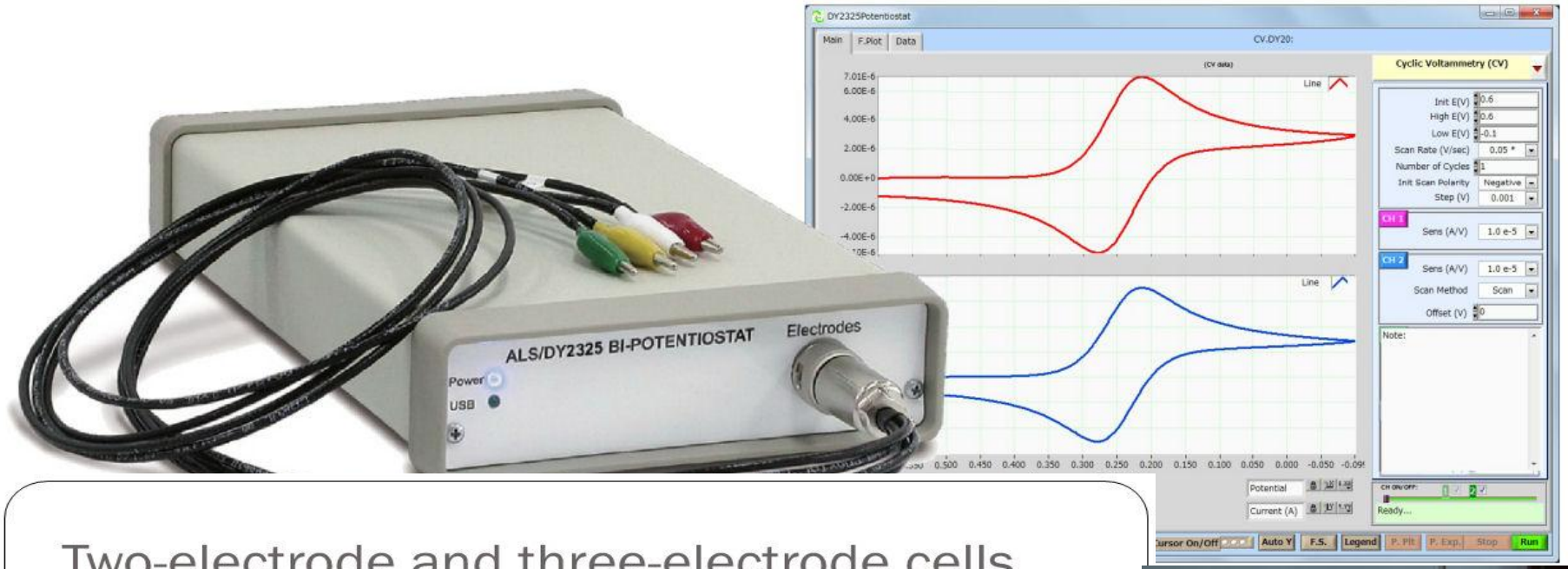
Working electrode: conductor whose potential is varied with time. At this electrode, reduction or oxidation of the investigate analyte takes place

Reference electrode: potential remains constant (Ag/AgCl electrode or calomel)

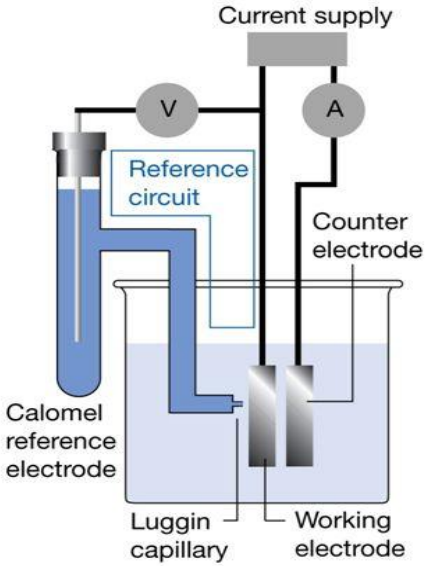
Counter electrode Metal wire or other conductor that completes circuit, Oposite reaction of that at the working electrode takes place at the counter electrode

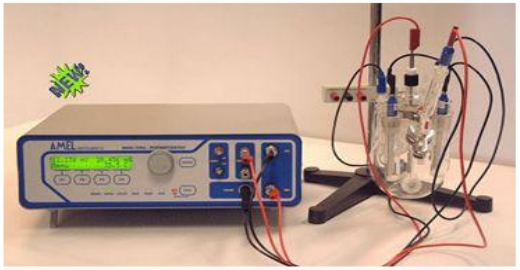
Supporting electrolyte: excess of nonreactive electrolyte (alkali metal) to conduct current

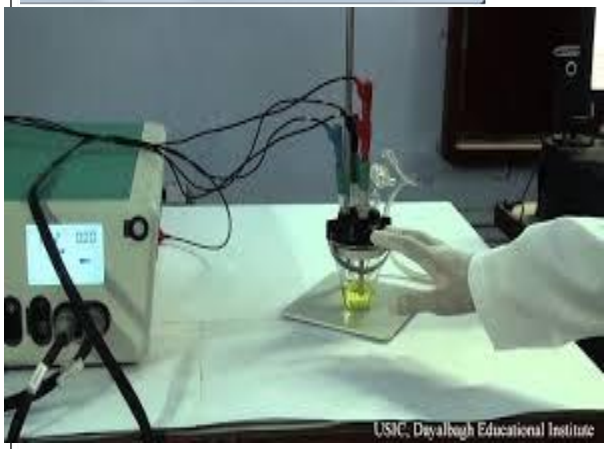


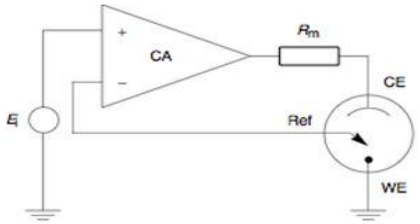


Two-electrode and three-electrode cells







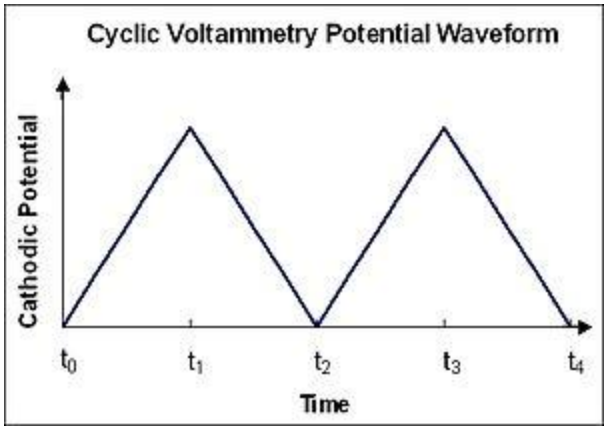


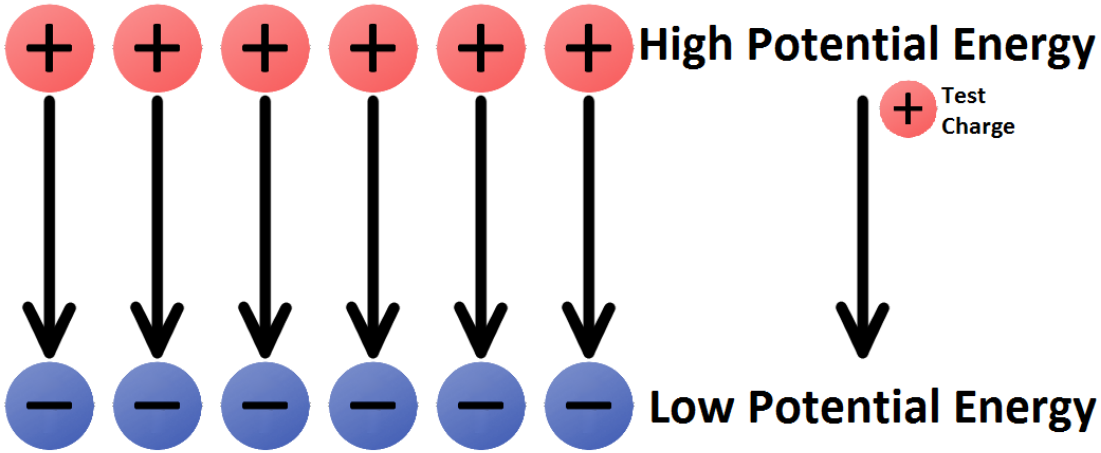
Electrochemical Cells and Instruments in Voltammetry

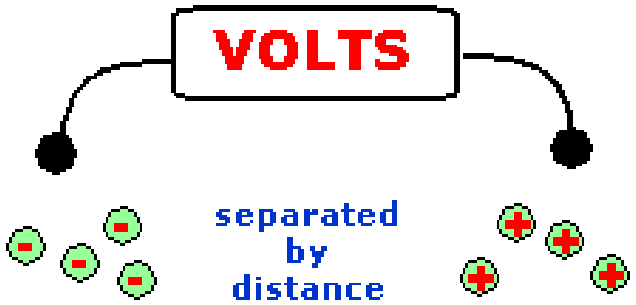
What is THE ELECTRICAL POTENTIAL?

Electrical potential (or electrical potential difference) is simply the MEASURE OF the ENERGY of ELECTRONS flowing between two systems that are close to eachother

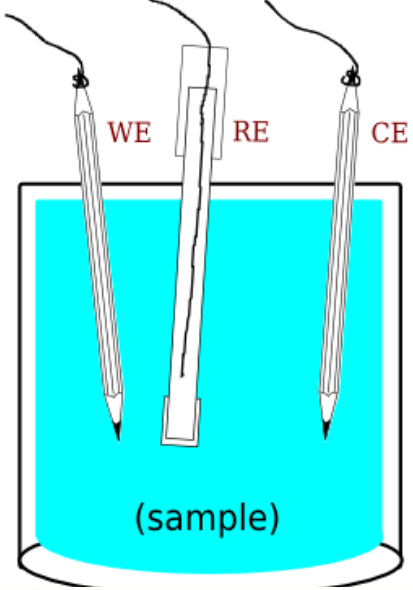
By changing the electrode potential, we actually affect the energy of ELECTRONS from the outher surface of a given electrode vs their environment





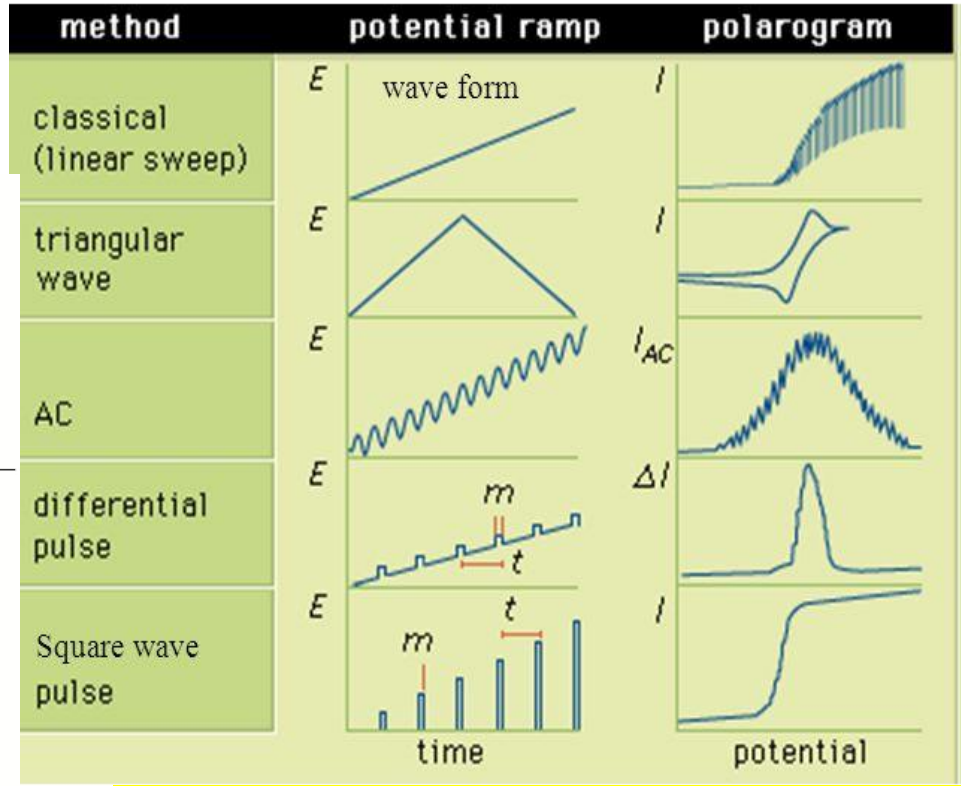


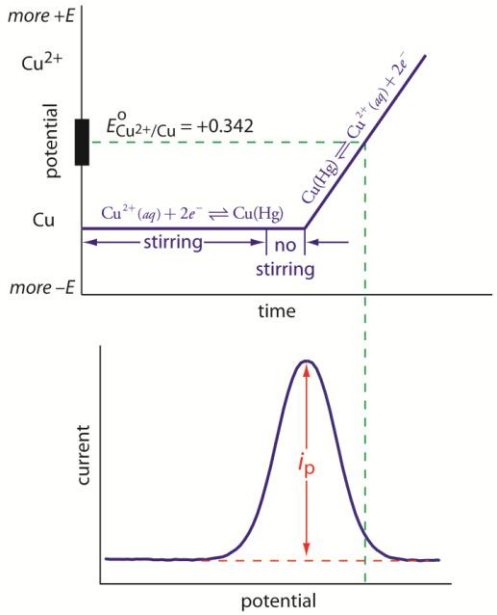
Potential Signals and resulting voltammograms of different voltammetric techniques

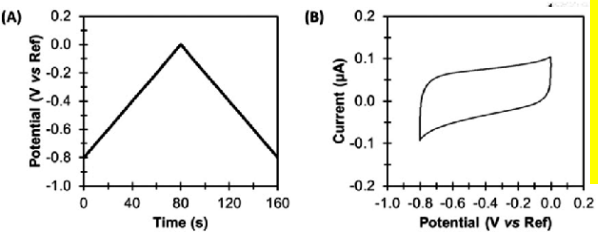


Excitation signals

In voltammetry, the voltage of the working electrode is varied systematically while the current response is measured. Several different voltage-time functions, called excitation signals, can be applied to the electrode.







***Important*!!!: Scan RATE (or rate of changing the potential with time) is the most important parameter affecting the features of voltammograms**

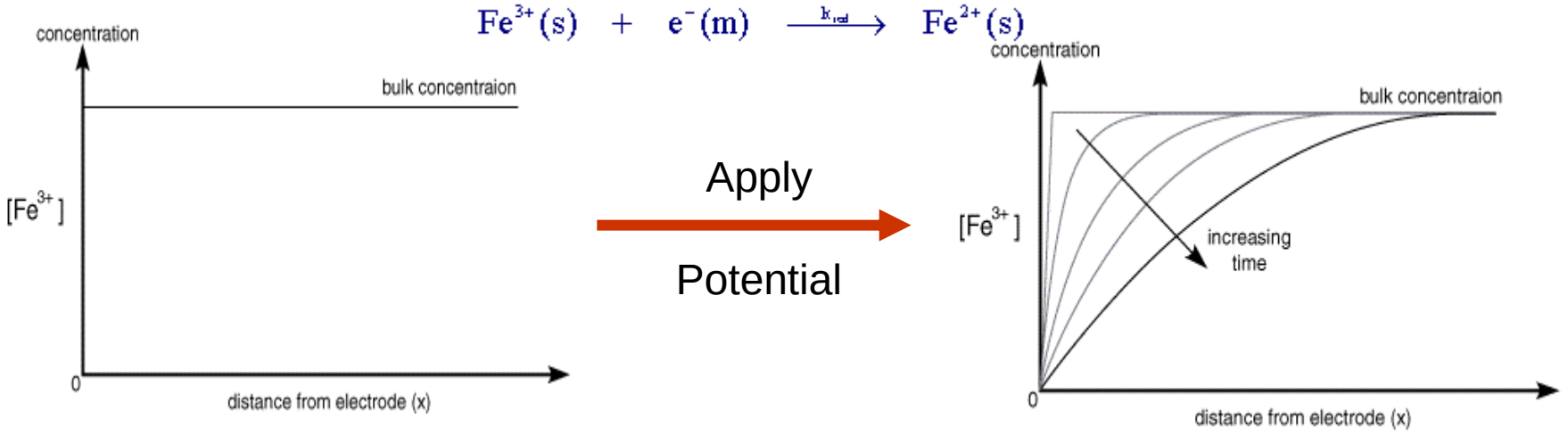
***Voltammetry* a successor of polarography-first reported in 1922 by Czech chemist Jaroslav Heyrovsky (polarography). Later given Nobel Prize for method in 1959.**

In every technique there must be an
Excitation Source: it is the electode potential set by outer source to the working electrode)

Applied potential is a function of concentration of Reduced and Oxidized Species at electrode based on Nernst Equation:

$$E_{electrode} = E^0 - \frac{0.0592}{n} \log \frac{(a_R)^r (a_S)^s \ldots}{(a_P)^p (a_Q)^q \ldots}$$

- reaction at the surface of the electrode takes place in the micrometer layer nearby electrode surface (or at the electrode surface attached)

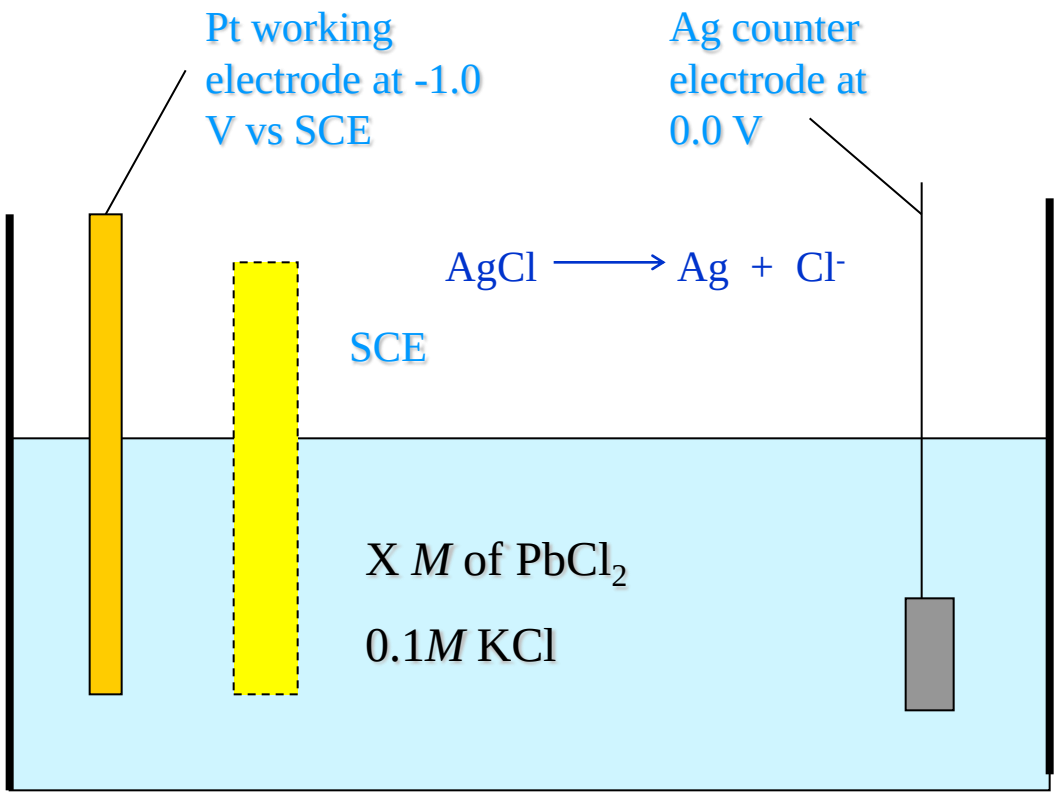


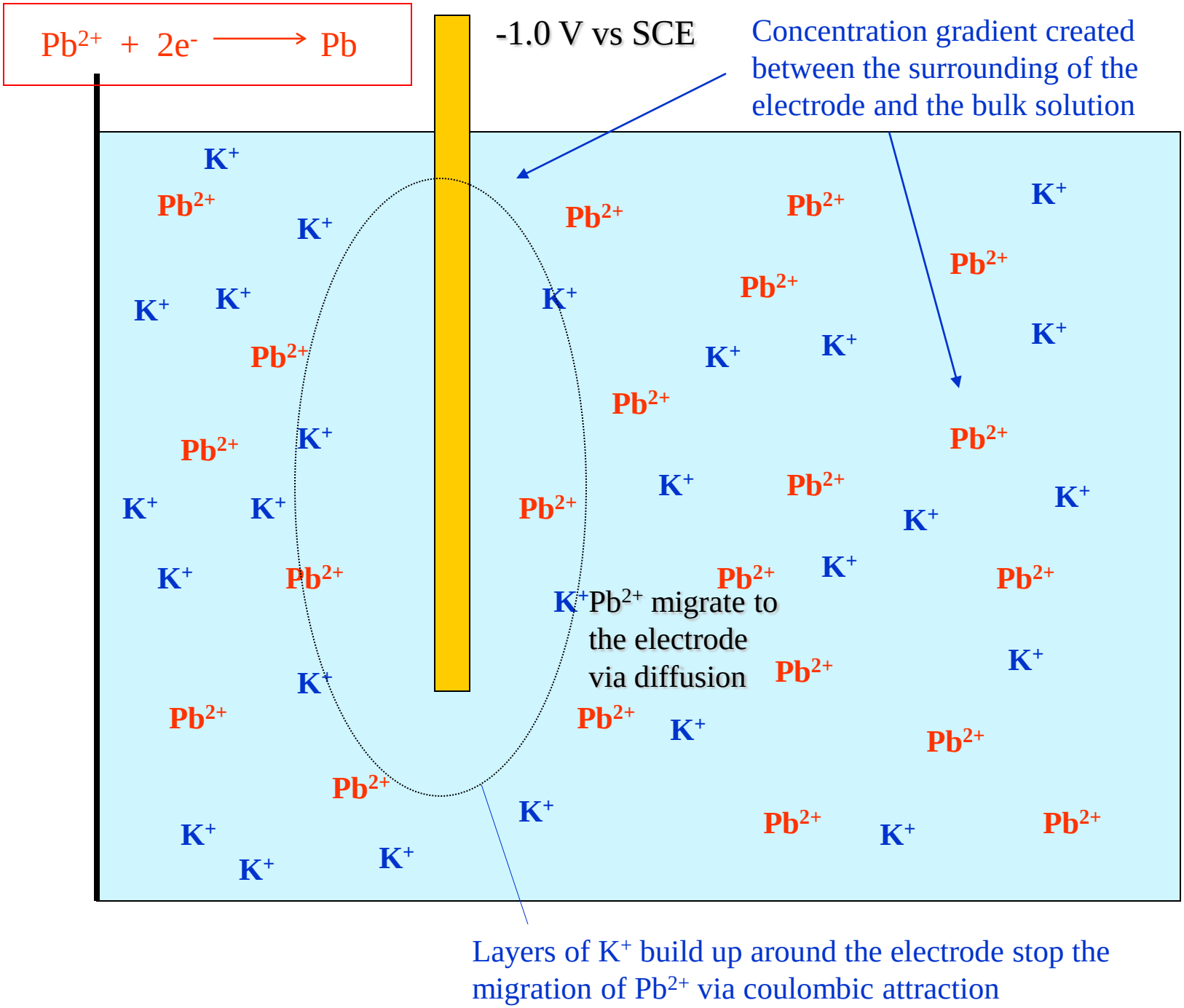
Voltammetric analysis-What Happens in Electrochemical Cell when potential is applied?

- Analyte selectivity is provided by the applied potential on the working electrode.
  - ♦ Electroactive species in the sample solution are drawn towards the working electrode where a half-cell redox reaction takes place.
  - ♦ Another corresponding half-cell redox reaction will also take place at the counter electrode to complete the electron flow.
  - ♦ The resultant current flowing through the electrochemical cell reflects the activity (i.e. ≈ concentration) of the electroactive species involved

$Pb^{2+} + 2e^- \longrightarrow Pb \quad E^O = -0.13$ V vs. NHE

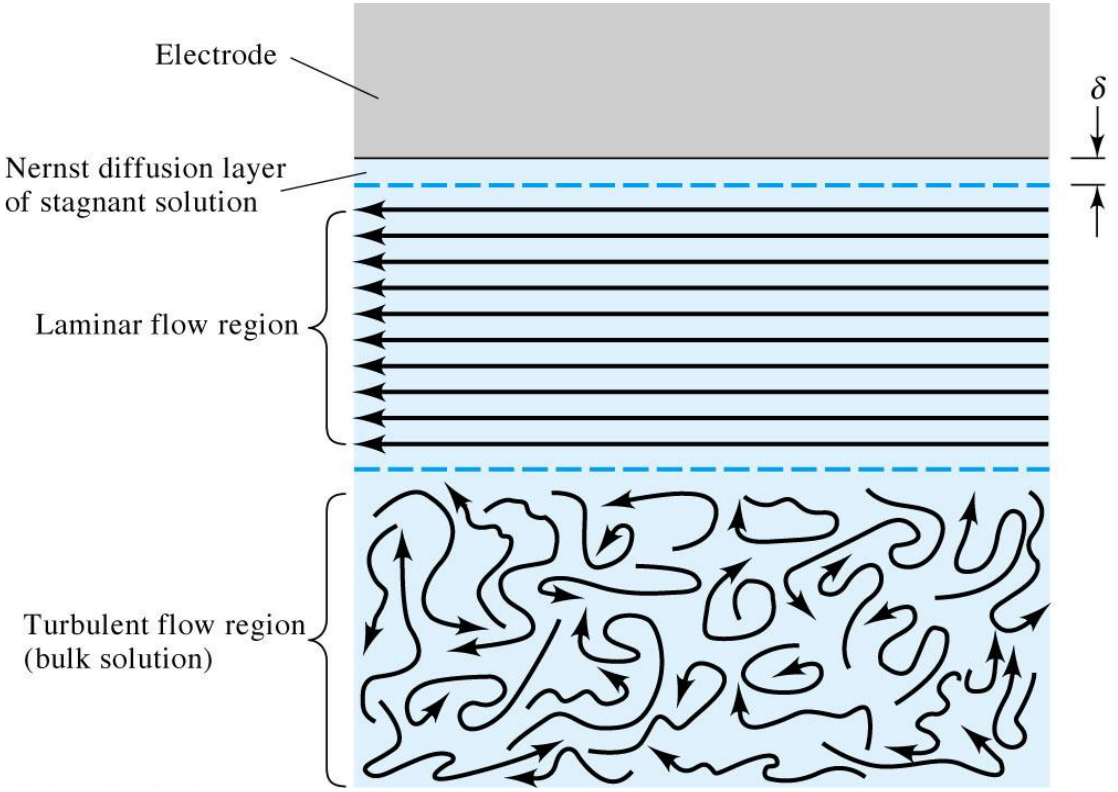
$K^+ + e^- \longrightarrow K \quad E^O = -2.93$ V vs. NHE




$Pb^{2+} + 2e^- \longrightarrow Pb$
-1.0 V vs SCE
Concentration gradient created between the surrounding of the electrode and the bulk solution
Pb^{2+} migrate to the electrode via diffusion
Layers of K^+ build up around the electrode stop the migration of Pb^{2+} via coulombic attraction

Current is measure of rate at which species can be brought to electrode surface

MASS TRANSPORT towards working Electrode surface happens when applied potential Changes the concentration of a given analyte in the vicinity of the working electrode surface



Three transport mechanisms:

(i) *migration* – movement of ions through solution by electrostatic attraction to charged electrode

(ii) *convection* – mechanical motion of the solution as a result of stirring or flow

(iii) *diffusion* – motion of a species caused by a concentration gradient

What Happens at the electrode surface and in the analyte concentration (present in the electrolyte solution) When potential is applied to the working electrode?

At Electrodes Surface: $M_{ox} + e^- \rightleftharpoons M_{red}$

$$E_{appl} = E^o - \frac{0.0592}{n} \log \frac{[M_{red}]_s}{[M_{ox}]_s}$$

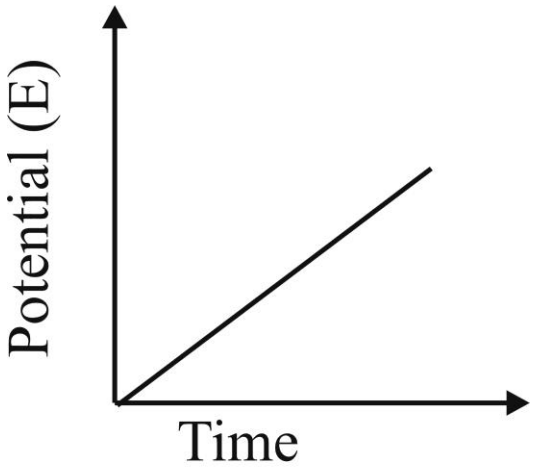
Applied potential

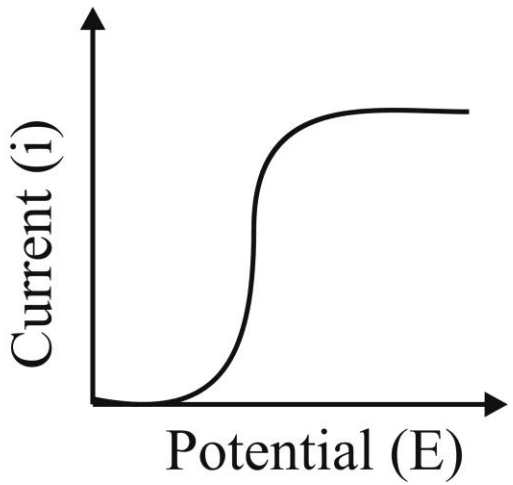
at surface of electrode

If $E_{appl} = E^o$:

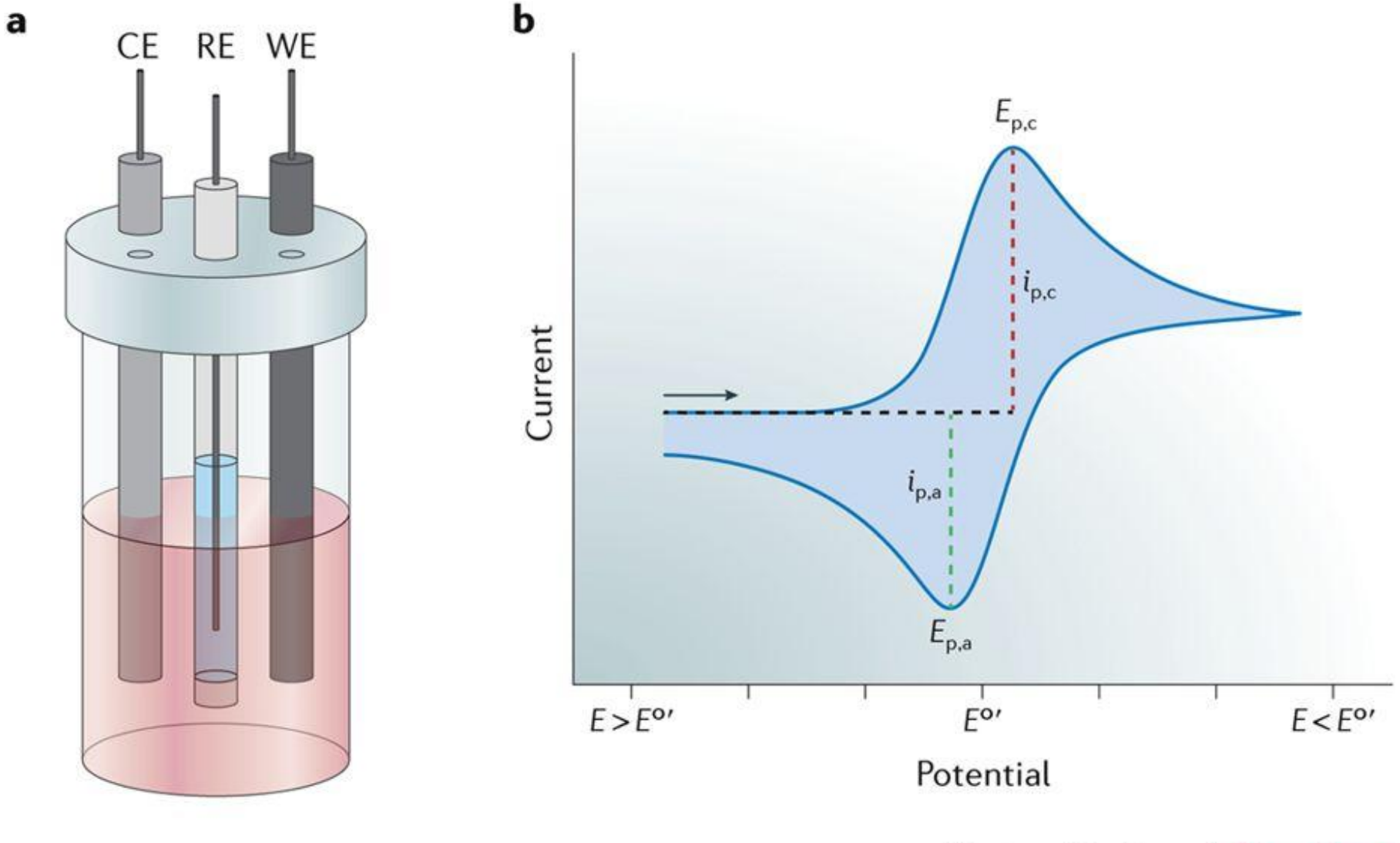
$$0 = \frac{0.0592}{n} \log \frac{[M_{red}]_s}{[M_{ox}]_s}$$

® $[M_{ox}]_s = [M_{red}]_s$





CYCLIC VOLTAMMETRY-Electrochemical SPECTROSCOPY
-most familiar technique in the family of voltammetric methods-
-gives insights into the mechanisms of various redox reactions-



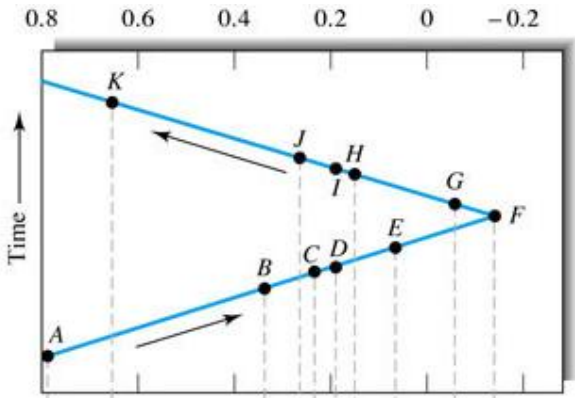
Nature Reviews | Chemistry

Cyclic Voltammetry

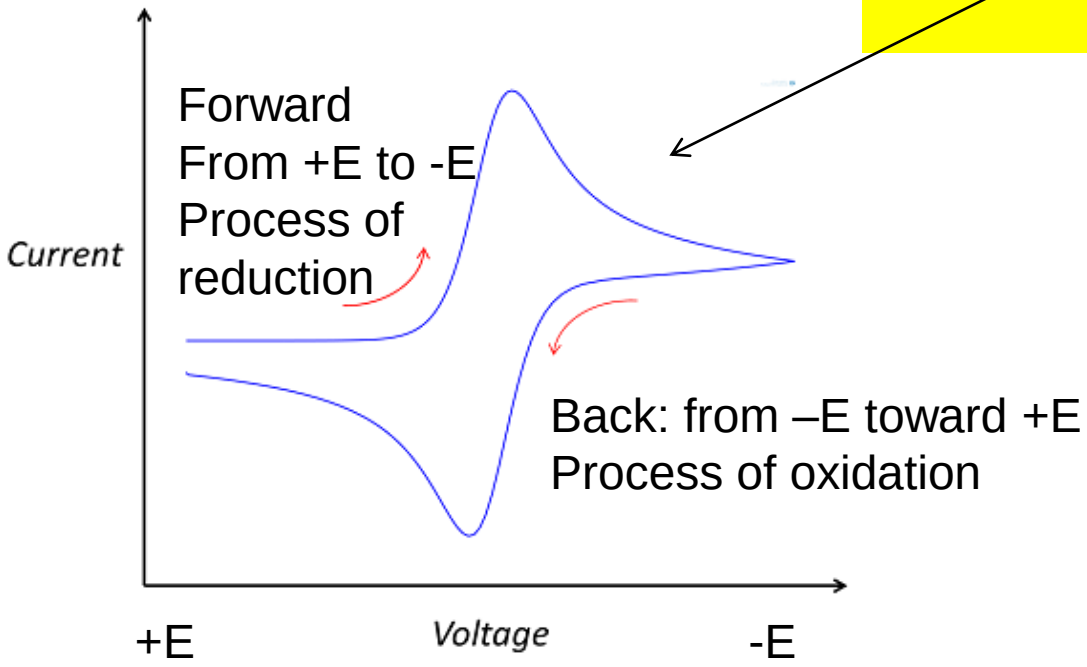
1) is a voltammetric Method used to look at mechanisms of redox reactions in solution.

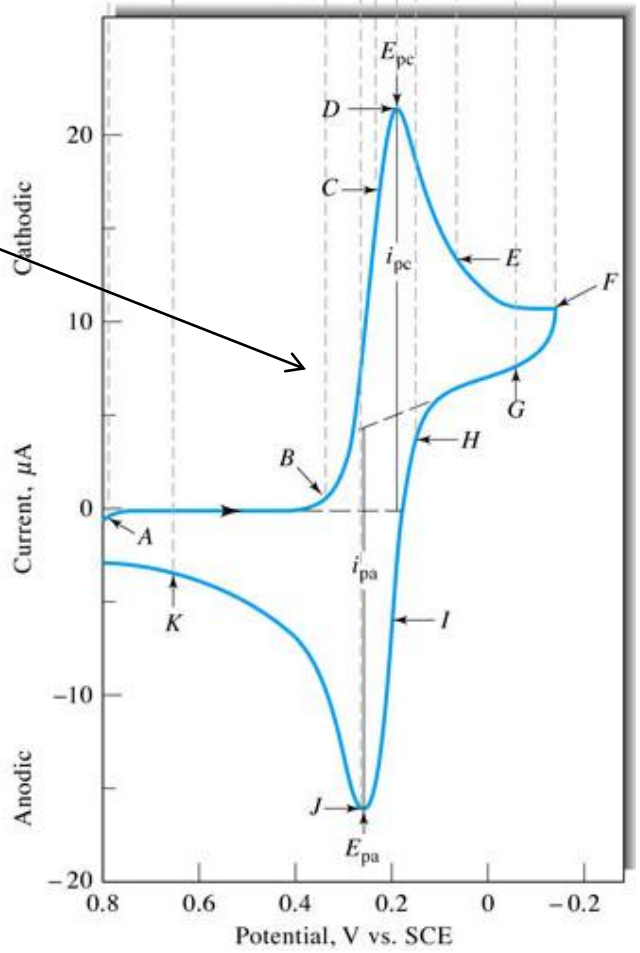
…but also for thermodynamic and kinetic measurements

2) triangular potential waveform for excitation



Cyclic voltammogram of a reversible redox reactic of simple diffusional Redox reaction

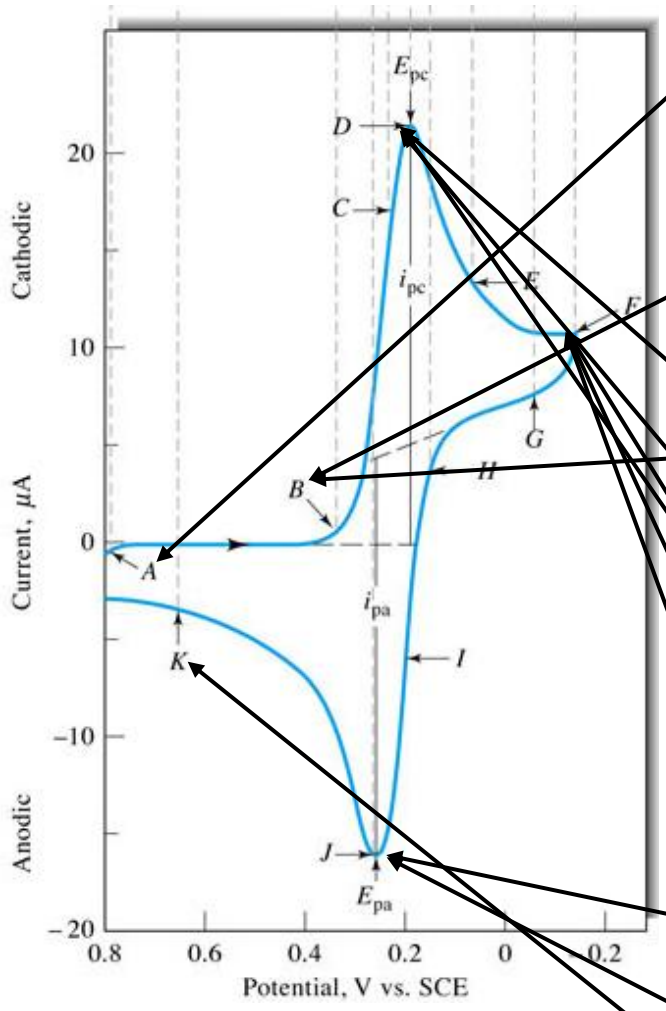




Practical Example: reduction of K3[Fe(CN)6]; explanation on what happens at every potential

Working Electrode is Pt & Reference electrode is SCE

6 mM $K_3Fe(CN)_6$ & 1 M KNO_3



A. Initial negative current due to oxidation of H_2O to give O_2

No current between A & B (+0.7 to +0.4V) no reducible or oxidizable species present in this potential range

B. At 0.4V, current begins because of the following reduction at the cathode:

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$$

B.-D. Rapid increase in current as the surface concentration of $Fe(CN)_6^{3-}$ decreases

D. Cathodic peak potential (E_{pc}) and peak current (i_{pc})

D.-F. Current decays rapidly as the diffusion layer is extended further from electrode surface

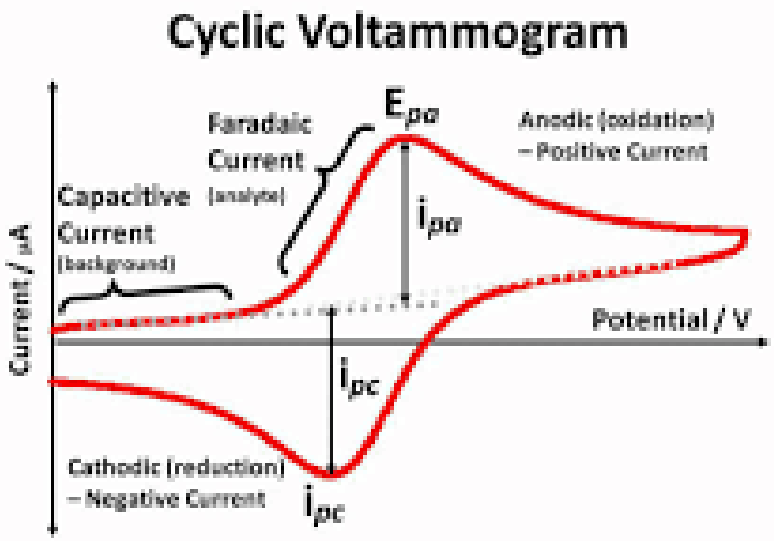
F. Scan direction switched (-0.15V), potential still negative enough to cause reduction of $Fe(CN)_6^{3-}$

F.-J. Eventually reduction of $Fe(CN)_6^{3-}$ no longer occurs and anodic current results from the reoxidation of $Fe(CN)_6^{4-}$

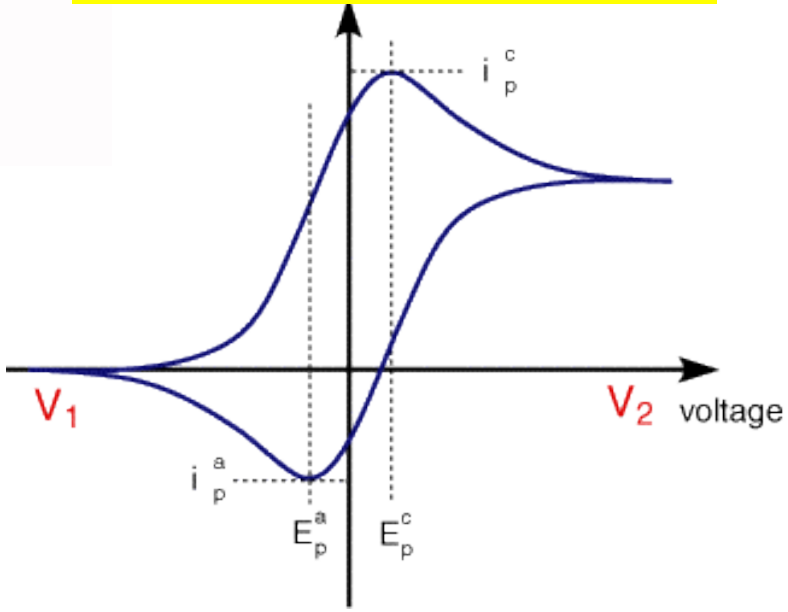
J. Anodic peak potential (E_{pa}) and peak current (i_{pa})

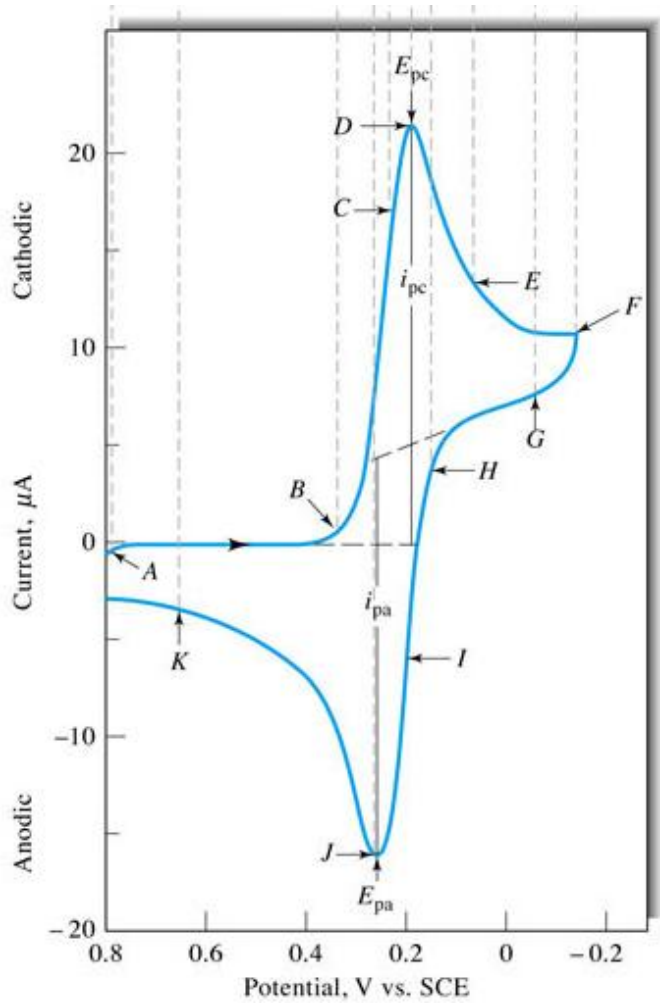
K. Anodic current decreases as the accumulated $Fe(CN)_6^{4-}$ is used up at the anodic reaction

What is important to recognize from the features of Cyclic voltammograms?



Simple redox reactions
Planar electrode
Mass transfer by diffusion
Reversible electron transfer
Thermodynamic parameters
Kinetic parameters
Mechanism
-analytical determination





Important Quantitative Information

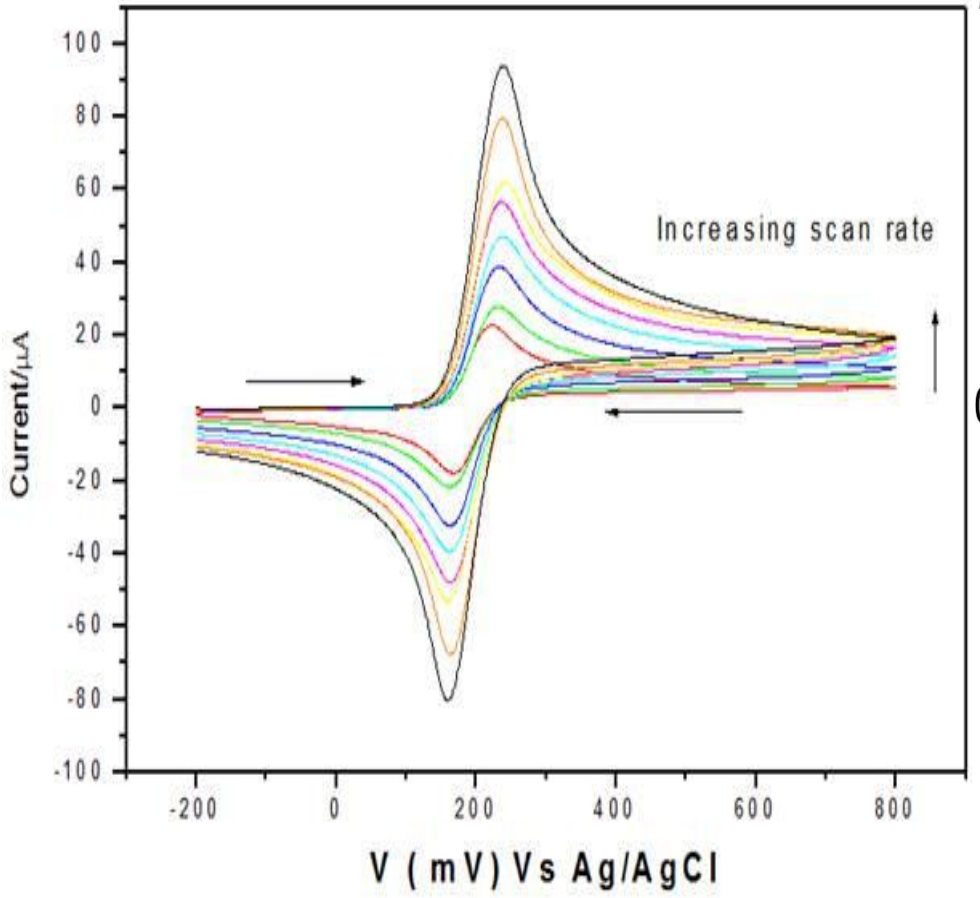
- i_{pc} 👉 i_{pa}
- $\Delta E_p = (E_{pa} - E_{pc}) = 0.0592/n$,
  where n = number of electrons in reaction
- E^0 = midpoint of $E_{pa} \rightarrow E_{pc}$
- $i_p = 2.686 \times 10^5 n^{3/2} A c D^{1/2} v^{1/2}$

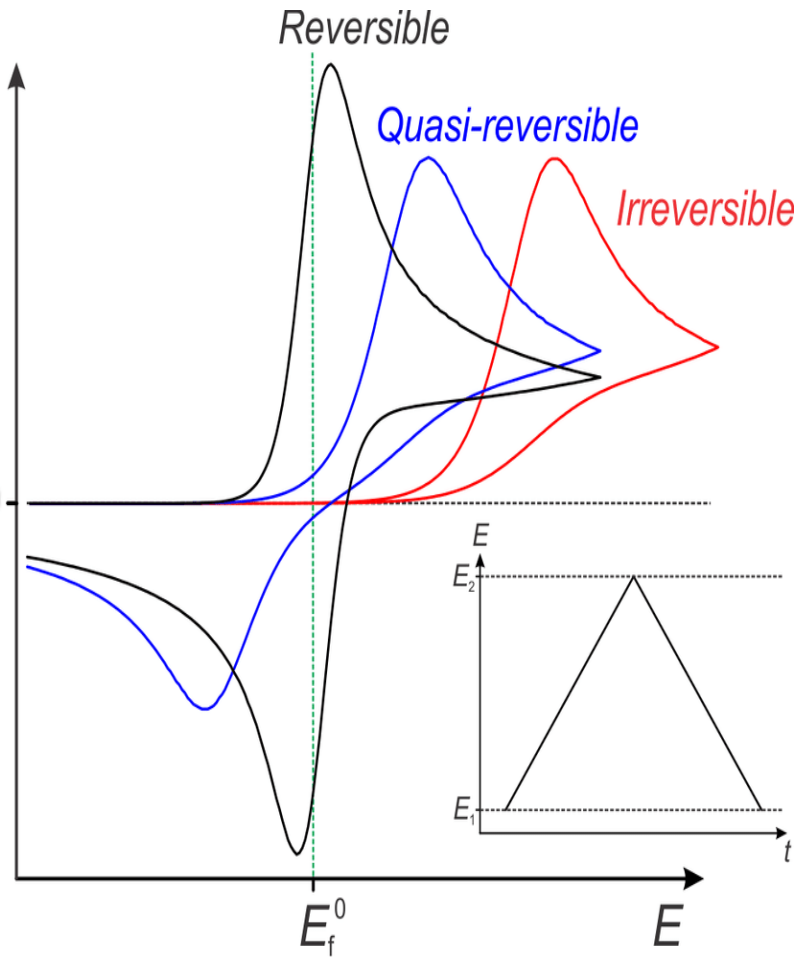
  - ***A*: electrode area**
  - ***c*: concentration**
  - **v: scan rate**
  - ***D*: diffusion coefficient**

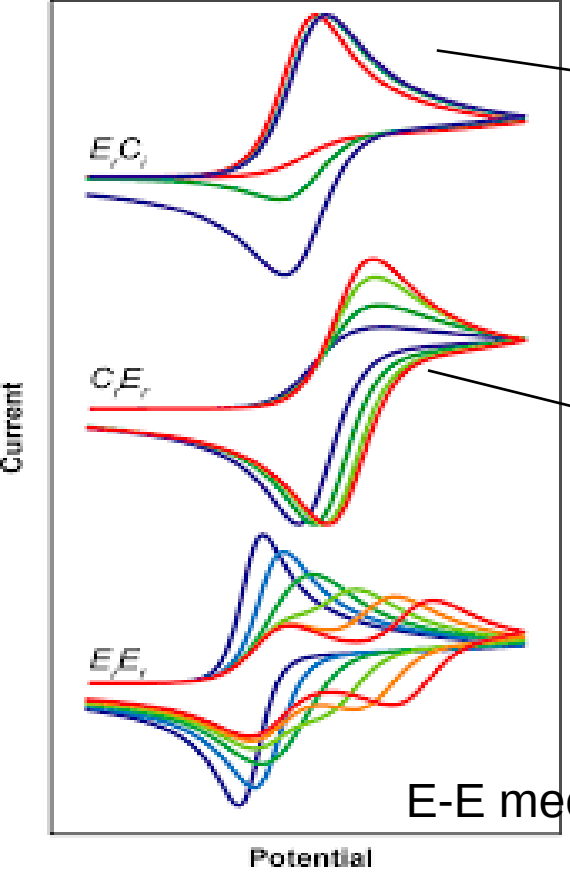
Thus,

- *can calculate standard potential for half-reaction*
- *number of electrons involved in half-reaction*
- *diffusion coefficients*
- *if reaction is reversible*

1. FEATURES of CYCLIC DIFFUSIONAL VOLTAMMOGRAMS OF SOME MOST COMMON REDOX MECHANISMS







E-E mechanism

$E \quad O + e \rightleftharpoons R$

$C \quad R \xrightarrow{k_{EC}} Products$

CYCLIC VOLTAMMETRY

Applications

E = redox step and C = chemical step

EC
- Redox step followed by chemical step

$O + ne^- \leftrightarrow R + A \rightarrow Z$

- R reacts chemically to produce Z
- Z is electroinactive
- Reverse peak is smaller since R is chemically removed

$i_{pa}/i_{pc} < 1$

s

CYCLIC VOLTAMMETRY

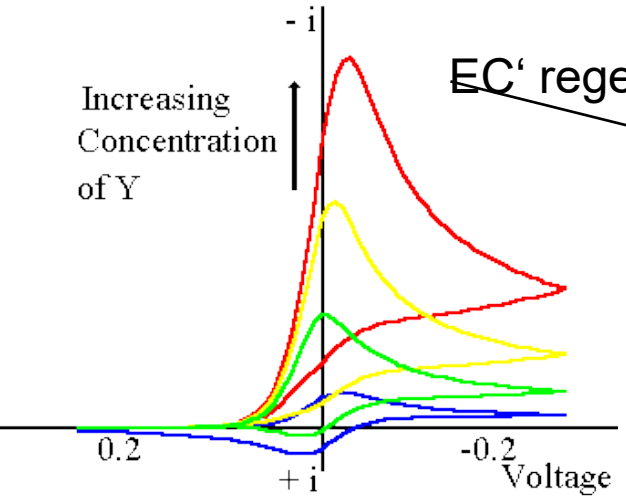
Applications

E = redox step and C = chemical step

CE
- Slow chemical reaction precedes the electron transfer step

$Z \rightarrow O + ne^- \leftrightarrow R$

$i_{pa}/i_{pc} > 1$ (approaches 1 as scan rate decreases)
i_{pa} is affected by the chemical step
i_{pc} is not proportional to $v^{1/2}$



EC‘ regenerative mechanism

CYCLIC VOLTAMMETRY

Applications

E = redox step and C = chemical step

EC
- Catalytic regeneration of O during a chemical step

$O + ne^- \leftrightarrow R + A \leftrightarrow O$

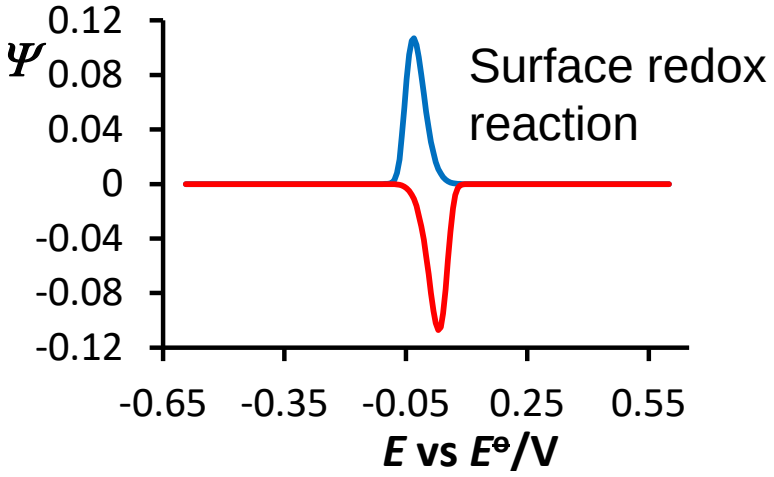
- Peak ratio is unity

Example
- Oxidation of dopamine in the presence of ascorbic acid

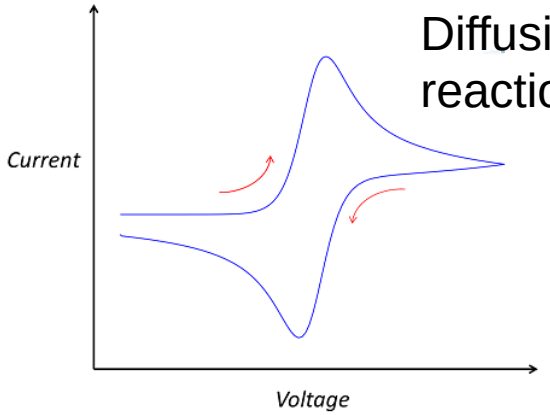
CYCLIC VOLTAMMETRY OF SURFACE REDOX REACTIONS

-NO DIFFUSION!!!

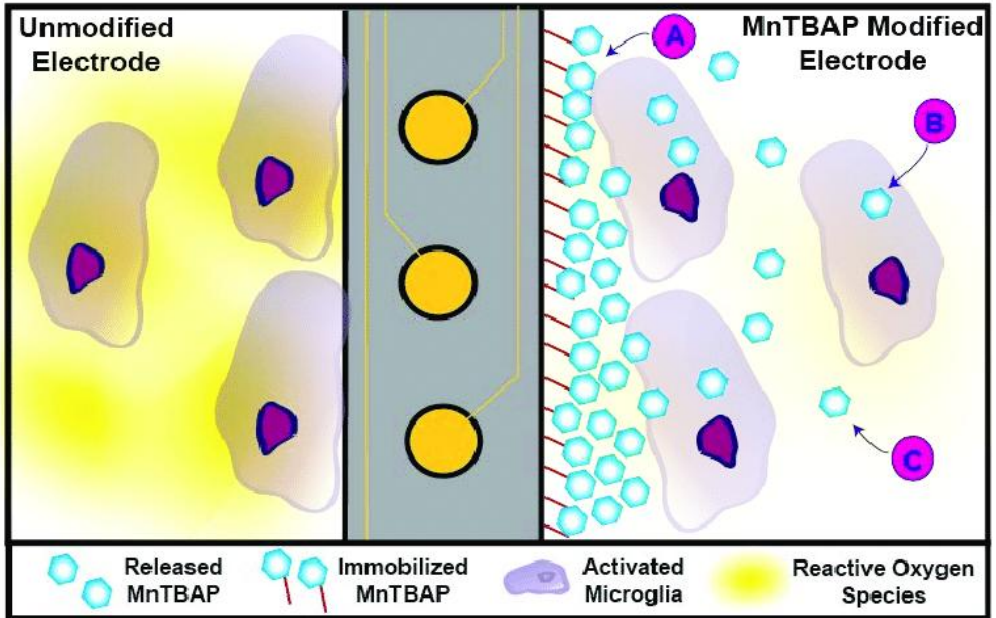
-The ANALYTE STAYS FIRMLY ADSORBED ON ELECTRODE SURFACE during all applied potentials!!!

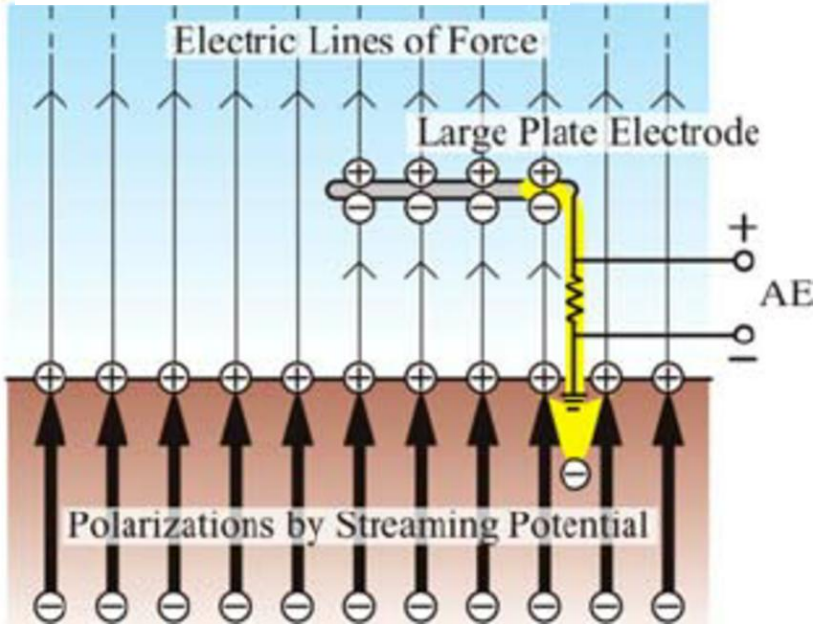


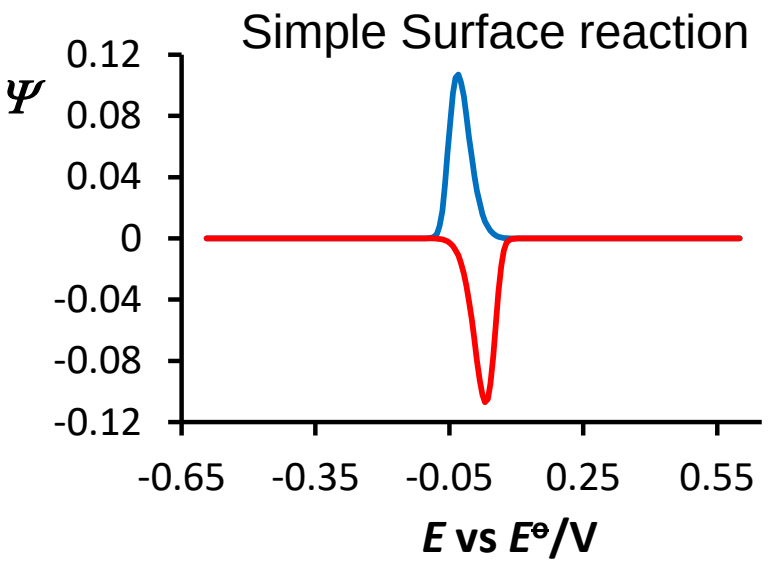
Surface redox reaction

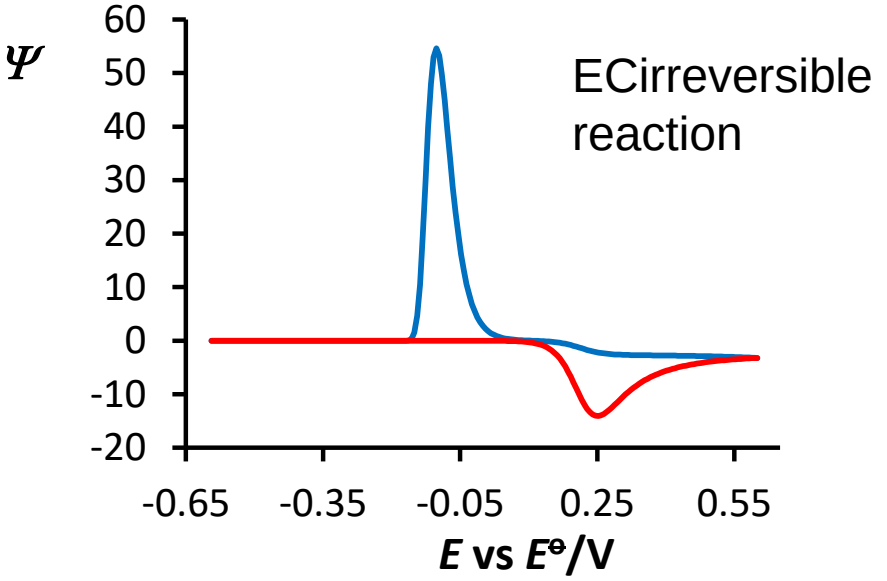


Diffusional redox reaction

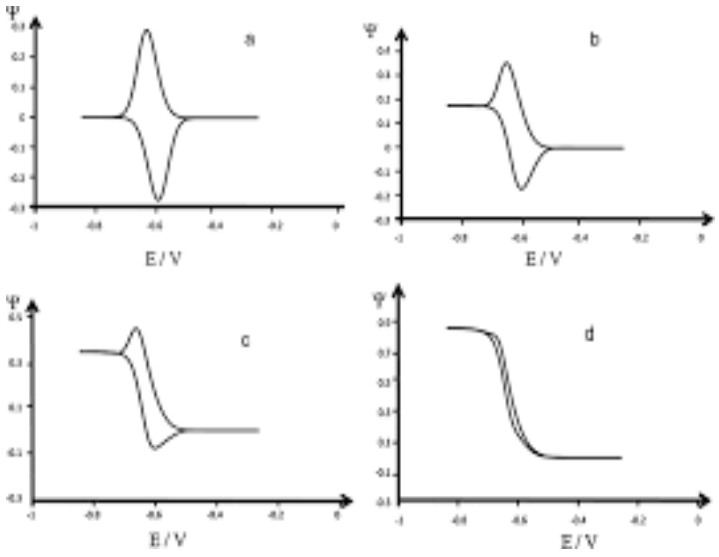


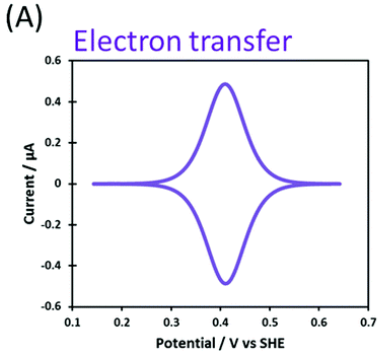


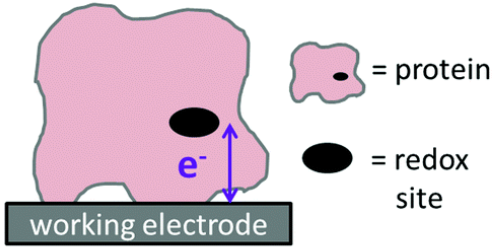


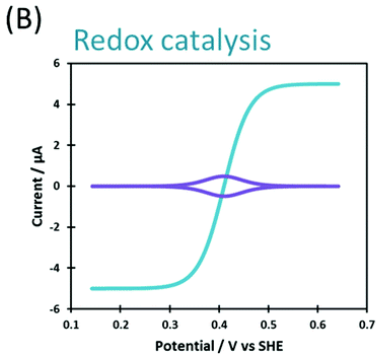


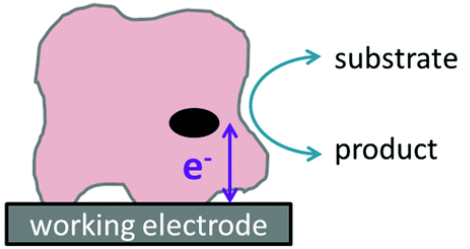
EC‘ regenerative catalytic mechanism







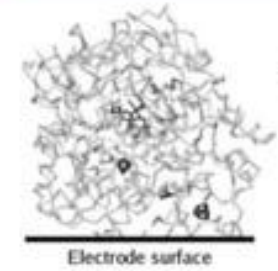


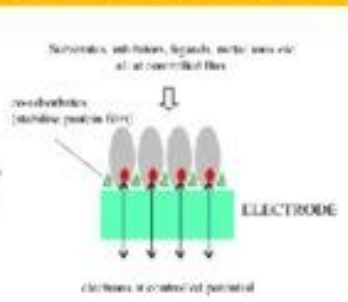


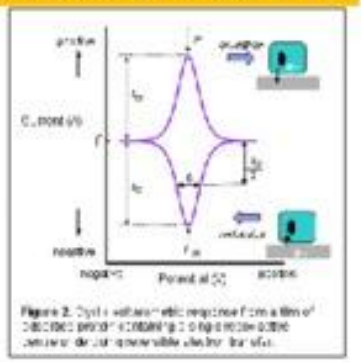
FUTURE PERSPECTIVES of Voltammetry

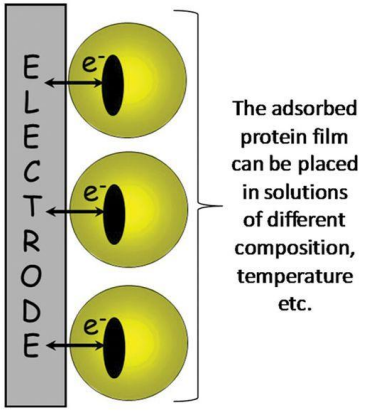
PROTEIN-FILM VOLTAMMETRY-ELECTROCHEMICAL SPECTROSCOPY FOR PROBING THE REDOX FEATURES OF BIOCATALYSTS

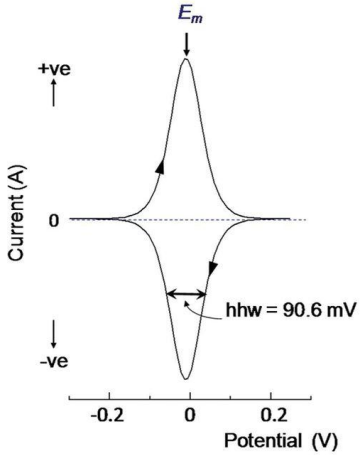
RUBIN GULABOSKI, GOCE DELCEV UNIVERSITY-STIP, MACEDONIA

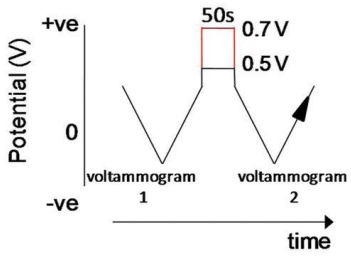


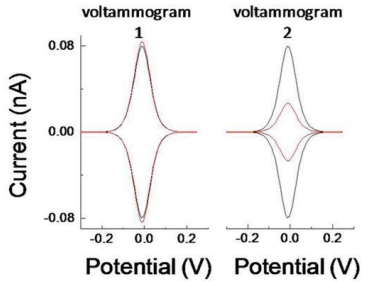








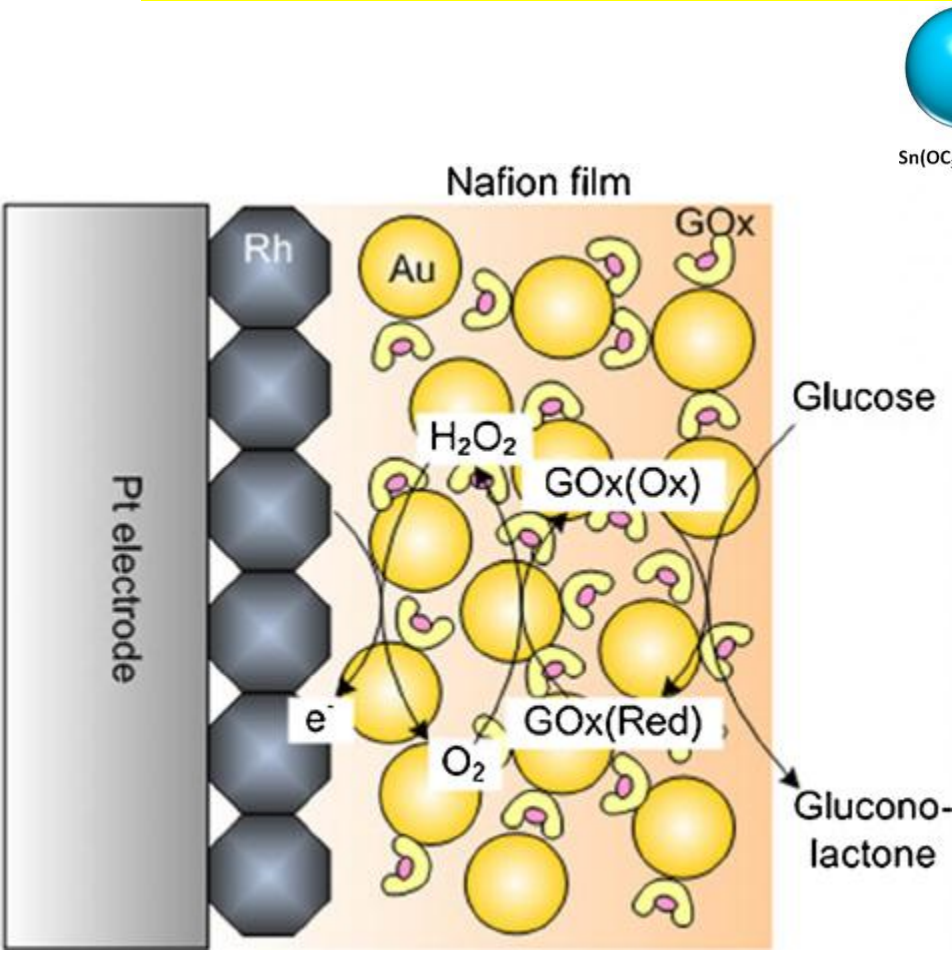


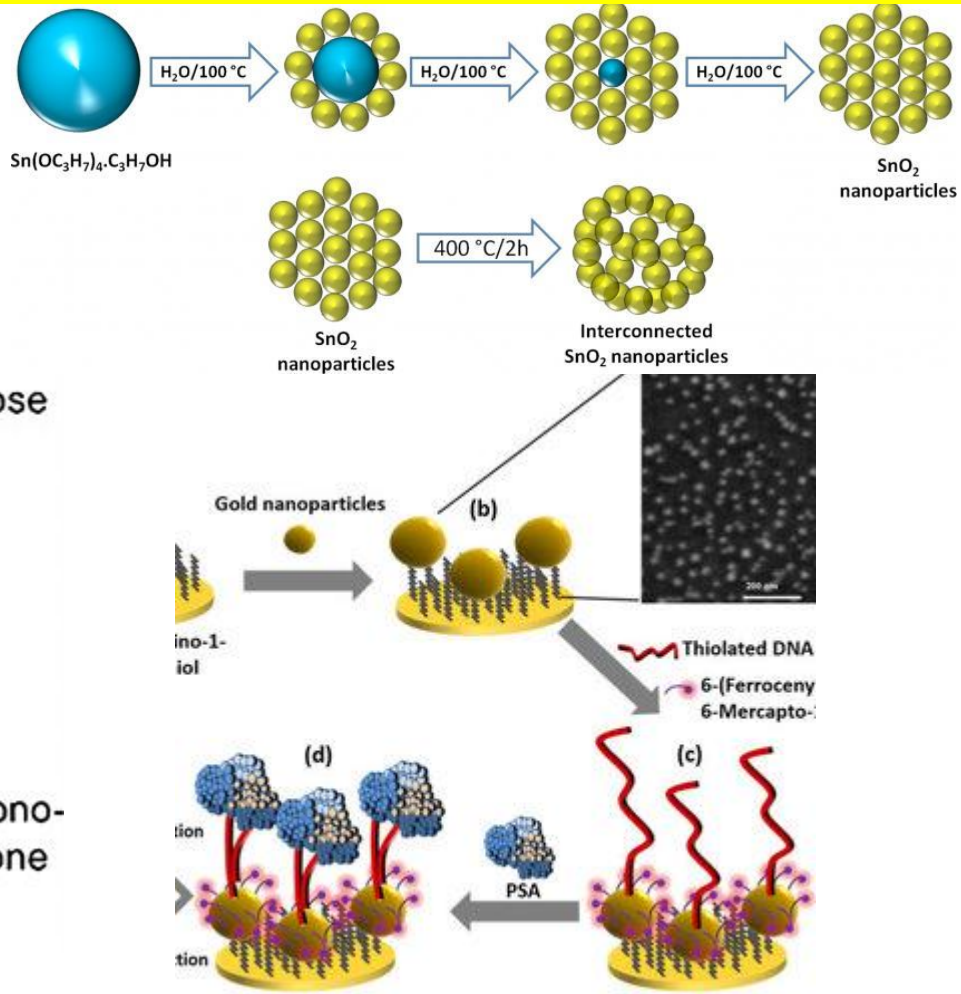


Protein-film voltammetry-Getting insights into Enzymes Redox Chemistry with Simple Experiments!!!

VOLTAMMETRY AT **NANOPARTICLES-FUTURE** SENSORS

-we must design nano-conductive materials that will allow larger Potential window and determination of various lipophilic analytes





2.) Current generated at electrode by this process is proportional to concentration at surface, which in turn is equal to the bulk concentration

For a planar electrode:

measured current *(i)* = $nFAD_A\left(\frac{\delta_{CA}}{\delta_x}\right)$

where:

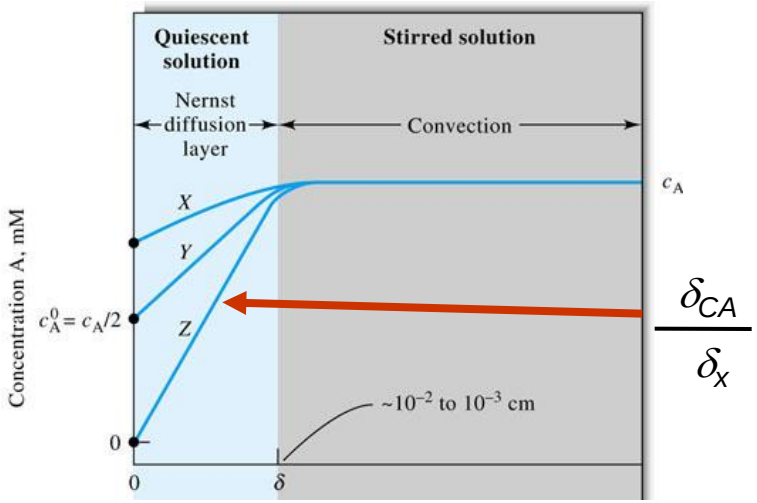
n = number of electrons in ½ cell reaction

F = Faraday's constant

A = electrode area (cm^2)

D = diffusion coefficient (cm^2/s) of A (oxidant)

$\frac{\delta_{CA}}{\delta_x}$ *= slope of curve between* $C_{Mox,bulk}$ *and* $C_{Mox,s}$



REFERENCES

1.R Gulaboski, S Petkovska, A Time-Independent Approach to Evaluate the Kinetics of Enzyme-Substrate Reactions in Cyclic Staircase Voltammetry, ANALYTICAL & BIOANALYTICAL ELECTROCHEMISTRY 10 (5), 566-575

2. S. Kostadinovic Velickovska, A. C. Mot, S. Mitrev, **R. Gulaboski**, L. Bruhl, H. Mirhosseini, R. Silaghi Dimitrescu, B. Matthaus, *Bioactive compounds and "in vitro" antioxidant activity 3 of some traditional and non-traditional cold-pressed edible oils from Macedonia*, ***J. Food Sci. Technol.*** (2018) doi: 10.1007/s13197-018-3050-0

3. R. Gulaboski, I. Bogeski, P. Kokoskarova, H. H. Haeri, S. Mitrev, M. Stefova, Marina, J. Stanoeva-Petreska, V. Markovski, V. Mirceski, M. Hoth, and R. Kappl, *New insights into the chemistry of Coenzyme Q-0: A voltammetric and spectroscopic study.* ***Bioelectrochem.*** 111 (2016) 100-108.

4. R. Gulaboski, V. Markovski, and Z. Jihe, *Redox chemistry of coenzyme Q—a short overview of the voltammetric features*, ***J. Solid State Electrochem.***,20 (2016) 3229-3238.

5. V. Mirceski, D. Guzijewski and R. Gulaboski, Electrode kinetics from a single square-wave voltammograms, Maced. J. Chem. Chem. Eng. 34 (2015) 1-12.

6. V. Mirceski, D. Guzijewski and **R. Gulaboski**, Electrode kinetics from a single square-wave voltammograms, ***Maced. J. Chem. Chem. Eng.*** 34 (2015) 1-12.

7. **Gulaboski** and V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, ***Electrochim. Acta***, *167 (2015) 219-225.*

8. V. Mirceski, Valentin and **R. Gulaboski,** *Recent achievements in square-wave voltammetry (a review).* ***Maced. J. Chem. Chem. Eng.*** 33 (2014). 1-12.

9. V. Mirceski, **R. Gulaboski**, M. Lovric, I. Bogeski, R. Kappl and M. Hoth, Square-Wave Voltammetry: A Review on the Recent Progress, ***Electroanal.*** 25 (2013) 2411–2422.

10. R. Gulaboski, I. Bogeski, V. Mirčeski, S. Saul, B. Pasieka, H. H. Haeri, M. Stefova, J. Petreska Stanoeva, S. Mitrev, M. Hoth and R. Kappl, "Hydroxylated derivatives of dimethoxy-1,4-benzoquinone as redox switchable earth-alkaline metal ligands and radical scavengers ***Sci. Reports***, 3 (2013) 1-8.

11. **R. Gulaboski**, V. Mirceski, I. Bogeski and M. Hoth, „Protein film voltammetry: electrochemical enzymatic spectroscopy. A review on recent progress„ ***J. Solid State Electrochem.*** 16 (2012) 2315-2328.

12. **R. Gulaboski,** P. Kokoskarova and S. Mitrev, "Theoretical aspects of several successive two-step redox mechanisms in

13. I. Bogeski, **R. Gulaboski***, R. Kappl, V. Mirceski, M. Stefova, J. Petreska and M. Hoth, „Calcium Binding and Transport by Coenzyme Q„ ***J. Am. Chem. Soc.*** 133 (2011) 9293-9303.

14. **R. Gulaboski** and L. Mihajlov, "Catalytic mechanism in successive two-step protein-film voltammetry—heoretical study in square-wave voltammetry", ***Biophys. Chem.***155 (2011) 1-9.

15. **R. Gulaboski**, M. Lovric, V. Mirceski, I. Bogeski and M. Hoth, Protein-film voltammetry: a theoretical study of the temperature effect using square-wave voltammetry., ***Biophys. Chem***. 137 (2008) 49-55.

16. **R. Gulaboski**, Surface ECE mechanism in protein film voltammetry—a theoretical study under conditions of square-wave voltammetry, ***J. Solid State Electrochem***. 13 (2009) 1015-1024

17. **R. Gulaboski**, E. S. Ferreira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garrau, V. Lippolis and A. F. Silva, Coupling of Cyclic Voltammetry and Electrochemical Impedance Spectroscopy for Probing the Thermodynamics of Facilitated Ion Transfer Reactions Exhibiting Chemical Kinetic Hindrances, ***J. Phys. Chem. C*** 112 (2008) 153-161.

18. **R. Gulaboski**, M. Lovric, V. Mirceski, I. Bogeski and M. Hoth, A new rapid and simple method to determine the kinetics of electrode reactions of biologically relevant compounds from the half-peak width of the square-wave voltammograms., ***Biophys. Chem***. 138 (2008) 130-137.

19. **R. Gulaboski**, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa and A. F. Silva, Probing of the Voltammetric Features of Graphite Electrodes Modified with Mercaptoundecanoic Acid Stabilized Gold Nanoparticles, ***J. Phys. Chem.*** *C* 112 (2008) 2428-2435.

20. R. **Gulaboski**, F. Borges, C. M. Pereira, M. N. D. S. Cordeiro, J. Garrido and A. F. Silva, Voltammetric insights in the transfer of ionizable drugs across biomimetic membranes: recent achievements., **Comb. Chem. High Throughput Screen.** 10 (2007) 514-526.

21. R. Gulaboski, V. Mirčeski, M. Lovrić and I. Bogeski, "Theoretical study of a surface electrode reaction preceded by a homogeneous chemical reaction under conditions of square-wave voltammetry." ***Electrochem. Commun***. 7 (2005) 515-522.
22. R. Gulaboski, V. Mirčeski, C. M. Pereira, M. N. D. S. Cordeiro, A. F Silva, F. Quentel, M. L'Her and M. Lovrić, "A comparative study of the anion transfer kinetics across a water/nitrobenzene interface by means of electrochemical impedance spectroscopy and square-wave voltammetry at thin organic film-modified electrodes." ***Langmuir*** 22 (2006) 3404-3412.
23. R. Gulaboski, C. M. Pereira. M. N. D. S. Cordeiro, I. Bogeski, E. Fereira, D. Ribeiro, M. Chirea and A. F. Silva, "Electrochemical study of ion transfer of acetylcholine across the interface of water and a lipid-modified 1,2-dichloroethane." ***J. Phys. Chem. B*** 109 (2005) 12549-12559.
24. F. Scholz and **R. Gulaboski** "Determining the Gibbs energy of ion transfer across water-organic liquid interfaces with three-phase electrodes." ***Chem. Phys. Chem***., 6 (2005) 1-13.
25. R. Gulaboski, V. Mirčeski, Š. Komorsky-Lovrić and M. Lovrić, "Square-Wave Voltammetry of Cathodic Stipping Reactions. Diagnostic Criteria, Redox Kinetic Measurements, and Analytical Applications", ***Electroanal.*** 16 (2004) 832-842.
26. V. Mirčeski and **R. Gulaboski**, "A Theoretical and Experimental Study of Two-Step Quasireversible Surface Reaction by Square-Wave Voltammetry" ***Croat. Chem. Acta*** 76 (2003) 37-48.
27. V. Mirčeski and **R. Gulaboski**, "The surface catalytic mechanism: a comparative study with square-wave and staircase cyclic voltammetry ", ***J. Solid State Electrochem***. 7 (2003) 157-165.

28. R. Gulaboski, V. Mirčeski and Š. Komorsky-Lovrić, “Square-Wave Voltammetry of a Second Order Cathodic Stripping Process Coupled by Adsorption of the Reacting Ligand”, ***Electroanal.*** 14 (2002) 345-354.

29. V. Mirčeski, M. Lovrić and **R. Gulaboski**, “Theoretical and experimental study of the surface redox reaction involving interactions between the adsorbed particles .under conditions of square-wave voltammetry.”, ***J. Electroanal. Chem***., 515 (2001) 91-99.

30. V. Mirčeski and **R. Gulaboski**, “Surface Catalytic Mechanism in Square-Wave Voltammetry”, ***Electroanal.*** 13 (2001) 1326-1334.

31. V. Mirčeski, **R. Gulaboski** and I. Kuzmanovski, “Mathcad-a Tool for Numerical Calculation of Square-Wave Voltammograms”, ***Bull. Chem. Technol. Macedonia*****,** 18 (1999) 57-64.

32. Scholz, F.; Schroeder U.; **Gulaboski R**. *Electrochemistry of Immobilized Particles and Droplets* Springer Verlag, New York, pp. 1-269, 2005.

33. **Gulaboski, R.** Pereira, C. M. In Electrochemical Methods and Instrumentation in Food Analysis, in Handbook of Food Analysis Instruments, Otles, S. (ed.) Taylor & Francis, 2015.

34. **Gulaboski R**. in Electrochemical Dictionary, A J. Bard, G. Inzelt, F. Scholz (eds.) Springer, 2nd Edition in 2012.

35. I. Bogeski, R. Kappl, C. Kumerow, **R. Gulaboski**, M. Hoth and B. A. Niemeyer "Redox regulation of calcium ion channels: Chemical and physiological aspects, ***Cell Calcium*** **50** (2011) 407-423.

36. R. Compton, Understanding Voltammetry, 2012.

37. V. Mirceski, S. Komorsky Lovric, M. Lovric, Square-wave voltammetry, Theory and Application, Springer 2008 (F. Scholz, Ed.)

Thickness of Diffusion Layer (δ):

$$i = \frac{nFAD_{ox}}{\delta}(c_{ox,\,bulk} - c_{ox,s})$$

- largest slope (highest current) will occur if:

$E_{appl} << E^o$ ($c_{ox,s}$  0)

then

$$i = \frac{nFAD_{ox}}{\delta}(c_{ox,\,bulk} - 0)$$

where:

$$k = \frac{nFAD_{ox}}{\delta}$$

so:

$$i = kc_{ox,bulk}$$

therefore:

current is proportional to bulk concentration

*- also, as solution is stirred, δ decreases and **i** increases*